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(54) LOW TEMPERATURE WATER GAS SHIFT REACTION

(54)

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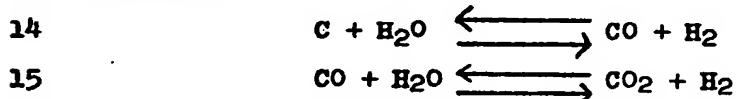
ABSTRACT:

ABSTRACT OF THE DISCLOSURE

Hydrogen is produced by reacting carbon monoxide with steam at a temperature of at least 200°F. in the presence of (1) at least one alkali metal compound derived from acids having ionization constants below 1×10^{-3} and (2) a metallic hydrogenation-dehydrogenation material. The ratio of metal component to the alkali metal compound, calculated on the basis of the oxides thereof, ranges from 0.0001 to about 10 parts by weight per part by weight of the alkali metal compound. The alkali metal compound may be impregnated on the hydrogenation-dehydrogenation component or may be mixed with or used in the presence of the metal component. A preferred catalyst combination is a potassium compound, such as potassium carbonate, mixed with cobalt-molybdenum on an alumina support.

1 This invention relates generally to a process for
2 producing hydrogen by reacting carbon monoxide with steam at
3 elevated temperatures in the presence of at least one alkali
4 metal compound and at least one metal hydrogenation-dehydro-
5 genation component. More particularly, the invention relates
6 to a process for producing hydrogen by reacting carbon monoxide
7 with steam at a temperature of at least 200°F. in the presence
8 of an alkali metal compound derived from an acid having an
9 ionization constant less than 1×10^{-3} with at least one metal
10 hydrogenation-dehydrogenation material.

11 The present invention relates to the preparation of
12 hydrogen from carbonaceous materials in accordance with the
13 equations:



16 It is well known to prepare hydrogen by reacting
17 carbonaceous materials, such as hydrocarbons with steam at
18 elevated temperatures of 1200° - 1400°F. or coal or coke with
19 steam at temperatures up to 2500°F. and then to react the
20 resulting mixture of CO and H₂ with more steam at lower tem-
21 peratures, for example, at 800° - 900°F. in the presence of
22 suitable catalysts to convert the carbon monoxide produced in
23 the first stage to carbon dioxide and additional hydrogen. The
24 second step, known as the water gas shift reaction, is limited
25 by equilibrium considerations and complete conversion of CO to
26 CO₂ is not realized. However, the concentration of CO in the
27 product when equilibrium is reached is highly dependent on the
28 temperature. Consequently conversions can be increased by
29 either removing the carbon dioxide and again contacting the CO
30 and steam with the catalyst in the same or subsequent stages
31 or by lowering the temperature.

1 The effect of temperature on the equilibrium constant

2 $K = \frac{(CO_2)(H_2)}{(CO)(H_2O)}$ is shown in the following table.

7	8	9	Concentration of CO at	
			10	11
12	13	14	15	16
°F.	K			
900	5.61			
800	9.03	5.19		
700	15.89	3.30	1.12	
600	31.44	1.77	0.56	
500	72.75			
400	206.8	0.29		

* A - 50% of a 1/1 H_2/CO mixture + 50% H_2O (steam)
 B - 30% of a 1/1 H_2/CO mixture + 70% H_2O (steam)

17 It is thus evident that less CO will remain unconverted
 18 and costly methods of operation will be avoided by operating
 19 at as low temperatures as possible, e.g., 300° - 700°F., pref-
 20 erably 400°- 600°F. Such low temperatures can be employed by
 21 the use of a catalyst consisting of copper deposited on zinc
 22 oxide. Unfortunately, however, this catalyst will not tolerate
 23 even traces of sulfur in the feed. Since coal and coke and
 24 heavy hydrocarbon feeds suitable for conversion to hydrogen con-
 25 tain appreciable amounts of sulfur, e.g., up to 5 to 10 wt. %,
 26 which is converted to hydrogen sulfide and even some small
 27 amounts of carbon disulfide and carbonyl sulfide, these feeds
 28 are precluded from use with the Cu-ZnO catalyst, and are limited
 29 to shift temperatures of 750° - 900°F. using a sulfur resistant
 30 catalyst such as Fe_2O_3 promoted with Cr_2O_3 .

31 It has now been found that gas mixtures containing
 32 carbon monoxide contaminated with relatively large amounts of
 33 sulfur can be converted to hydrogen economically by reaction
 34 with steam at a temperature of at least 200°F: in the presence
 35 of (1) at least one alkali metal compound, said compound being
 36 derived from an acid having an ionization constant less than
 37 about 1×10^{-3} , and (2) a hydrogenation-dehydrogenation com-
 38 ponent. The alkali metal compound (Group IA compound) and the

1 hydrogenation-dehydrogenation component may be supported on a
2 carrier together or separately. In addition, the alkali metal
3 compound may be impregnated on the hydrogenation-dehydrogena-
4 tion component. Suitable hydrogenation-dehydrogenation com-
5 ponents include: (a) Group VIII noble metals, in particular,
6 rhodium, ruthenium, palladium, osmium, iridium and platinum
7 metals and compounds thereof; (b) non-noble metal materials
8 including vanadium, molybdenum, cobalt, tungsten metals and
9 compounds thereof including mixtures thereof, in particular,
10 the oxides and sulfides; and (c) mixtures of one or more vana-
11 dium, molybdenum, cobalt and tungsten metals or compounds
12 (oxides or sulfides) with one or more nickel, iron or chromium
13 materials, e.g., nickel, iron or chromium metals or compounds
14 (oxides or sulfides) thereof.

15 At least a portion of the non-noble catalyst species
16 (categories (b) and (c) above) should exist in a sulfided form.
17 Such catalysts are particularly suitable for use with feeds
18 containing sulfur. However, these catalyst compositions may
19 also be used with sulfur-free feeds. When sulfur-containing
20 feeds are used, the non-noble metal catalyst may be sulfided
21 in situ by passing the feed over the oxide or other compound
22 which is then converted at least partially to a sulfide. The
23 noble metal containing catalysts are at least partially deact-
24 ivated through contact with sulfur. Hence, these catalysts
25 should be used with substantially sulfur-free feedstocks.

26 The ratio of hydrogenation-dehydrogenation component
27 to alkali metal compound is a critical feature of the instant
28 invention. Maximum catalyst activity is encountered when the
29 ratio of metal component to alkali metal compound varies from
30 about 0.001 to about 10 parts by weight per part by weight of
31 alkali metal compound, the weight ratios being calculated on
32 the basis of the oxides of each constituent. When noble metal

1 based catalysts are used, the ratio of metal component to alk-
2 ali metal compound, calculated on the basis of the oxides
3 thereof, desirably varies from about 0.0001:1 to about 10:1.
4 For purposes of calculating weight ratios, the metals are
5 assumed to exist in only the following oxide forms: CoO, MoO₃,
6 WO₃, V₂O₅, Fe₂O₃, NiO, Cr₂O₃, RuO₃, RhO₂, PdO, OsO₃, Ir₂O₃ and
7 PtO₂.

8 The figure is a plot of the relative activities of
9 various shift catalysts as a function of the weight ratio of
10 the hydrogenation-dehydrogenation component to the alkali metal
11 component of the catalyst.

12 The first stage reaction in the preparation of hydro-
13 gen consists in reacting coal, coke or heavy feeds at 1000°-
14 2500°F. with steam with or without the presence of hydrogen or
15 the reaction of natural gas or other hydrocarbons with steam
16 in the presence of reformer catalysts containing nickel, cobalt,
17 etc. promoted with magnesia, alumina, thoria and similar
18 oxides and supported, if desired, on an inert base at tempera-
19 tures of 1200° - 1600°F. Hydrogen, carbon dioxide and carbon
20 monoxide are obtained with a high ratio of CO to CO₂.

21 In accordance with my earlier findings, the second
22 stage, or shift reaction, in which the carbon monoxide formed
23 in the first stage is reacted with more steam at 300° - 700°F.,
24 preferably 400° - 600°F., may be carried out in the presence
25 of a cesium compound, derived from an acid with a pKa less than
26 1 x 10⁻³, supported on a carrier. These catalysts are affected
27 to some extent by sulfur but are sufficiently resistant to sul-
28 fur so that acceptable conversion of CO to CO₂ can be obtained.

29 The present invention makes it possible not only to
30 overcome the effect of sulfur on the alkali metal compounds but
31 also enables substantially complete conversion of carbon mon-
32 oxide to carbon dioxide to be achieved in one step at low

1 temperatures, an accomplishment which has heretofore been im-
2 possible in the presence of sulfur. These results are obtained
3 in accordance with the present invention by carrying out the
4 reaction in the additional presence of from about 0.001 to 10
5 parts by weight of a non-noble metal hydrogenation-dehydrogena-
6 tion catalyst component per weight of alkali metal (based upon
7 the weight of the oxides thereof) without reference to any
8 support which may be used. The use of these catalysts in con-
9 junction with the alkali metal salt enables more complete con-
10 version of the carbon monoxide to carbon dioxide even in the
11 presence of sulfur and thus affords vast economic savings since
12 a costly step of removing the carbon dioxide is avoided.

13 While it is not intended to be limited by any theory
14 concerning the mechanism of the reaction, it is believed that
15 the alkali metal component in the presence of water vapor
16 (steam) exists as a liquid phase in contact with the surface
17 of the hydrogenation-dehydrogenation component. It is believed
18 that the aqueous alkali metal phase converts the carbon mon-
19 oxide to formate and the hydrogenation-dehydrogenation catalyst
20 surface converts the formate into CO_2 and H_2 . Thus the inter-
21 action between the two types of catalysts brings about a vast
22 synergistic effect on catalytic activity. Nevertheless, in
23 the preferred embodiment of this invention, the reaction con-
24 ditions are such that the process reactants, specifically the
25 process steam, are present in the reaction zone in predominantly
26 the vapor phase. If liquid phase conditions exist, the propor-
27 tion of the steam present in the liquid phase is relatively
28 small compared to the total amount of steam employed in the
29 process.

30 Suitable alkali metal components include the carbonate,
31 bicarbonate, biphosphate, sulfide, hydrosulfide, silicate, bi-
32 sulfite, aluminate, hydroxide, acetate, tungstate, etc. of

1 sodium, potassium, lithium, rhubidium and cesium. In addition,
2 the alkali metal salts of organic acids such as acetate are
3 equally suitable. Actually the alkali salt of any acid which
4 has an ionization constant of less than 1×10^{-3} may be used.
5 The potassium and cesium salts, in particular potassium and
6 cesium carbonate, are most preferred.

7 It has been discovered that at least a portion of the
8 weak acid alkali metal salts are converted to the correspond-
9 ing alkali metal carbonate during the course of the shift re-
10 action. Additionally, salts of relatively unstable strong
11 acids, such as nitric acid, are also converted, at least par-
12 tially, to the carbonate. Hence, in most instances, the ul-
13 timate catalyst specie is believed to be the alkali metal car-
14 bonate. Therefore, the alkali metal catalyst constituent may
15 be any material that is at least partially converted to the
16 alkali carbonate during the course of the shift reaction.

17 The hydrogenation-dehydrogenation component of the
18 catalyst system may be noble metal materials, in particular,
19 ruthenium, palladium, osmium and platinum metals. Non-noble
20 metal materials, in particular sulfided metals, are highly
21 effective catalysts. Vanadium, molybdenum, cobalt, tungsten
22 and mixtures thereof, alone or in combination with nickel, iron
23 or chromium compounds, are the preferred non-noble catalyst
24 compositions. Examples of useful heavy metal catalyst com-
25 ponents include molybdenum-chromium, tungsten-chromium, cobalt-
26 nickel, cobalt-iron, molybdenum-tungsten, vanadium-tungsten,
27 platinum-tungsten, iridium-cobalt, rhodium-cobalt, vanadium-
28 cobalt, molybdenum, cobalt-iron, nickel-tungsten, vanadium,
29 platinum, palladium, cobalt-nickel-molybdenum, cobalt-iron-
30 molybdenum, etc.

31 If the above non-noble metals are used with sulfur-
32 containing feeds, they may be initially employed in the form

1 of the oxide or other compound easily sulfided. These com-
2 pounds are then sulfided in situ during the passage of the
3 sulfur-containing feed over them. Cesium or potassium carbon-
4 ate or acetate combined with cobalt-molybdenum oxides and/or
5 sulfides is a particularly effective catalyst combination.
6 Hereinafter, the non-noble catalysts will be referred to as the
7 metal without reference to how it is combined since the actual
8 composition, prior to shift reaction, is, for example, cobalt
9 oxide-molybdenum oxide-aluminum oxide and the like. Under the
10 reaction conditions the non-noble metal based catalyst usually
11 exists in a partially reduced and sulfided state which is
12 difficult to define stoichiometrically and thus a description
13 using the active metallic elements is as accurate as any. It is
14 believed that the active noble metal catalyst specie is the
15 metal itself. Typically, noble metal containing catalysts are
16 introduced into the reactor in the oxide form. The noble metal
17 oxide is thereafter converted to the active catalyst species
18 during the course of the shift reaction.

19 The catalytically active metal components may be used
20 either supported or unsupported and in the former case the
21 nature of the carrier is not critical. Suitable carriers in-
22 clude alumina having an extremely broad range of surface areas,
23 such as gamma and alpha aluminas. Other suitable support mate-
24 rials include silica, silica-alumina, e.g., silica-alumina
25 cogel cracking catalysts; zeolites such as faujasite, erionite,
26 and the like; activated carbon, coconut charcoal, magnesia,
27 boria, thoria, titania, zirconia and the like. Particularly
28 suitable gamma and alpha-alumina catalyst supports are avail-
29 able commercially. Such supports may be prepared by a variety
30 of methods. For example, they may be prepared by hydrolyzing
31 an aluminum alcoholate which may have been prepared in accord-
32 ance with the disclosures of U.S. Patent 2,636,865. They may

1 also be prepared by precipitating a hydrous alumina from an
2 aqueous solution of an aluminum salt, preferably AlCl_3 . A third
3 method of preparation comprises dissolving metallic aluminum
4 in weakly acidified water, preferably acidified with an organic
5 acid, such as acetic acid, in the presence of mercury or com-
6 pound thereof, and thereafter gelling the alumina sol thus
7 formed. The hydrous alumina prepared by any of the foregoing
8 procedures is subsequently dried and calcined at temperatures
9 between 600° and 1200°F., preferably between 900° and 1000°F.

10 The extent of the surface area of the support material
11 employed is believed to be a factor in the performance of the
12 total catalyst system. Desirably, the catalyst support has a
13 relatively low surface area, e.g., less than about 50-100 m^2/gram ,
14 as determined by the BET Method. Low surface area supports,
15 such as alpha alumina having a surface area of less than about
16 5 - 20 m^2/gram (BET Method), are effective catalyst carriers,
17 in particular, for noble metal-containing catalysts.

18 The catalyst components can be incorporated on the
19 support in any conventional manner. Preferably, the hydrogena-
20 tion-dehydrogenation components are placed on the support first
21 and this combination is then calcined, e.g., at 1000° - 1200°F.,
22 to convert the metals to the stable oxide forms. Then the alk-
23 ali metal, e.g., cesium or potassium carbonate, is impregnated
24 onto the support using aqueous or alcoholic media and the
25 catalyst simply dried. The impregnation operation can be car-
26 ried out before the remaining catalyst is introduced into the
27 reactor or after the remaining catalyst constituents are in
28 place within the reaction zone. In general, the carrier mate-
29 rial is impregnated with a solution containing the desired com-
30 pound. The finished catalyst is then sulfided in a known man-
31 ner, e.g., by passing over the catalyst a mixture of hydrogen
32 and hydrogen sulfide, carbon disulfide, butyl mercaptan and

1 the like. However, it may be sulfided in situ as described
2 above. Alternatively, sulfur can be placed on the catalyst by
3 introducing the alkali compound as the alkali sulfide.

4 Alternatively, the various components may be mixed
5 by mechanical means, such as by dry mixing. Good catalysts
6 can be obtained by fine milling of a cobalt-molybdenum catalyst
7 supported on alumina and mixing the powder obtained with a pow-
8 dered alkali metal compound such as cesium carbonate. The re-
9 sultant mixture, after the addition of a lubricant such as
10 stearic acid or graphite, is compressed into pellets which can
11 be calcined and sulfided.

12 The hydrogenation-dehydrogenation component is gen-
13 erally used in amounts varying from about 0.0001 to about 5 -
14 10 parts by weight based on the alkali metal compound. In the
15 case of non-noble metal catalysts, the metal constituent/alkali
16 metal compound weight ratio preferably varies from about 0.01
17 to about 5.0 parts by weight of hydrogenation-dehydrogenation
18 material and, most preferably, from 0.1 to 3.0 parts by weight
19 of non-noble metal catalyst per part by weight of alkali metal
20 compound, exclusive of any carrier which might be used to sup-
21 port either or both components. All components are calculated
22 on the basis of the oxide thereof.

23 When a carrier is used the ratio of catalyst compo-
24 nents (metal material and alkali compound) to carrier is not
25 critical but may range from about 90 wt. % to about 0.5 wt. %,
26 however, it has been found most desirable to use amounts of
27 from about 50 to about 1 wt. %, all based on total catalyst
28 including the carrier. Hydrogenation-dehydrogenation catalysts
29 which have been found particularly effective contain cobalt
30 oxide and molybdenum oxide on gamma alumina prior to sulfiding.
31 Particularly suitable ranges of catalyst components are from
32 about 0.1 to about 10 wt. % cobalt oxide and from about 1 to

1 about 25 wt. % molybdenum oxide. Most suitable are hydrogena-
2 tion-dehydrogenation components present in an amount of from
3 1 to about 5 wt. % cobalt oxide and from 5 to about 15 wt. %
4 molybdenum oxide. This catalyst component can then be impreg-
5 nated with about 5 to about 80 wt. % of alkali metal compound
6 and sulfided to make the final catalyst. Alternatively, the
7 alkali metal compound may be itself supported independently of
8 the hydrogenation-dehydrogenation component, both of which may
9 be mixed together and then sulfided to make the catalyst
10 composition.

11 The shift process is preferably carried out continu-
12 ously. The gaseous hourly space velocity can vary within wide
13 limits. Gaseous hourly space velocities of at least 300 vol-
14 umes of feed per volume of supported catalyst per hour (V/V/Hr),
15 preferably space velocities between about 300 and 30,000
16 (V/V/Hr), measured on the basis of dry gas under standard con-
17 ditions are particularly suitable for most applications. The
18 process may be carried out at higher gaseous hourly space
19 velocities if desired.

20 Referring now more specifically to the shift process,
21 except for the low temperature, with its favorable effect on
22 reaction equilibrium, resulting from the practice of this inven-
23 tion, water gas shift reactions are well known. Carbon monoxide
24 or a gas containing 0.1% or more carbon monoxide by volume, and
25 steam in an amount of 1-100 volumes per volume of carbon mon-
26 oxide, are introduced into a shift converter and passed over
27 the alkali metal and hydrogenation-dehydrogenation catalyst at
28 a temperature between 200° and 700°F. The pressure is prefer-
29 ably in the range of 200 to 1500 pounds per square inch gauge
30 (psig), although it may vary from atmospheric to 3000 psig or
31 more. However, the exact pressure and temperature conditions

1 must be maintained above the dew point of the steam in the mix-
2 ture. The process is particularly effective when the feed con-
3 tains sulfur. In fact, the presence of sulfur in the feed
4 actually results in increased conversions in many cases. If
5 necessary, the catalyst may be regenerated by oxidation and
6 resulfiding.

7 The use of the catalyst system of this invention leads
8 to an extremely high heat release. Heat control may therefore
9 be an important consideration in designing process equipment.
10 Heat problems may be avoided with the use of a fluidized process
11 in place of the fixed bed process normally used for shift
12 reaction. If a fixed bed process is used, the high heat re-
13 lease might be accommodated by the use of an inert diluent or
14 by pseudo staging of the catalyst beds by diluting the catalyst
15 along the length of the catalyst beds.

16 Typical results of operations in accordance with the
17 process of this invention are given in the following examples.
18 It will be evident that the examples are merely illustrative of
19 the invention and no undue limitation is imposed thereby. In
20 all cases herein the analyses of the hydrogenation-dehydrogena-
21 tion component are calculated on the basis of the metals ex-
22 pressed as the oxides and the alkali metal component expressed
23 as the oxides.

24 EXAMPLE 1

25 A gas mixture consisting of approximately 46% hydro-
26 gen, 53% carbon monoxide and about 1% H₂S was used as feed.
27 This gas feed was passed through a reactor containing a cata-
28 lyst at 550 psig at such a rate as to maintain an exit dry gas
29 product rate of 2700 V/V/Hr. measured at room temperature and
30 1 atmosphere of pressure and together with the feed gas was fed
31 steam in the mole ratio of one mole per mole of dry product gas.
32 The catalyst consisted of cobalt-molybdenum dispersed on gamma

1 alumina having a surface area of 200-400 M²/g., the cobalt con-
 2 tent corresponding to 3.5 wt. % of CoO and the molybdenum con-
 3 tent corresponding to 13 wt. % MoO₃ and which was impregnated
 4 with 44 - 48 wt. % of cesium acetate in an aqueous solution
 5 (1.7 x 10⁻³ moles per cc catalyst volume) and dried at about
 6 150°C. The catalyst was then sulfided in situ by passing the
 7 feed over the catalyst for about an hour at a temperature of
 8 625°F. The following results were obtained.

9 TABLE I

10	Run No.	1	2	3
11	Metals	CoMo	CoMo	None
12	Alkali metal compound	Cs Acetate	Cs Acetate	Cs Acetate
13	γ-alumina support	Type A	Type B	Type B

14 % CO in Product

15	Temp. °F.	Pressure psig		
17	625	550	1.16	48.61
18	525	550	0.53	0.54
19	475	550	0.43	
20	425	550	0.32	0.40
21	425	200	0.31	0.23
22	350	200	20.57	
23	350	0	45.54	41.35

24 The above data show that a mixture of cesium acetate
 25 and cobalt-molybdenum is an extremely effective and efficient
 26 catalyst for catalyzing the water gas shift reaction down to
 27 temperatures as low as 350°F. This compares very favorably
 28 with the results obtained with cesium acetate alone under the
 29 same conditions where 48.61% of carbon monoxide remained in
 30 the product at 625°F. Feed gas and product gas analyses are
 31 expressed as mol. %.

32 EXAMPLE 2

33 The experiment of Example 1 was repeated except that
 34 the cobalt and molybdenum were used separately. The results
 35 are shown in Table II.

1 TABLE II

2 Run No. 4
 3 Metals Co (4.4 wt.% CoO) 5
 4 Alkali Cs Acetate Mo (11 wt.% MoO₃)
 Cs Acetate

5 % CO in Product

6 Temp.	7 Pressure		
°F.	psig		
8 625	550	4.10	1.53
9 525	550	32.83	11.56

10 These two examples illustrate the enhanced effectiveness of the cobalt-molybdenum combination in contrast to each 11 component alone, even though all of these systems are effective 12 catalysts in the invention.

13 EXAMPLE 3

14 The experiment of Example 1 was repeated showing the 15 effect of varying the alkali metal component when using cobalt- 16 molybdenum. The results are reported in Table III.

17 TABLE III

18 Run No. 6 7
 19 Metals CoMo CoMo
 20 Alkali K Acetate Cs₂CO₃
 21 (1.7 x 10⁻³ 10⁻⁴
 22 moles/cc catalyst) (8.7 x 10⁻⁴
 23 moles/cc catalyst)

24 % CO in Product

25 Temp.	26 Pressure		
°F.	psig		
27 625	550	1.19	1.28
28 525	550		0.59
29 475	550		
30 425	550	0.39	0.37
31 425	200	0.77	0.35
32 350	200		
33 350	0		43.67

34 The above data show that potassium acetate is substantially as effective as cesium acetate down to temperatures 35 as low as 425°F. and that cesium carbonate is just as effective.

36 EXAMPLE 4

37 The experiment of Example 1 was again repeated to 38 show the effect of changing the non-noble metal constituent. 39 The results are shown in Table IV.

1 TABLE IV

2	Run No.	9	10
3	Metals	FeMo	NiMo
4	Alkali	Cs Acetate	Cs Acetate
<u>% CO in Product</u>			
6	Temp.	Pressure	
7	<u>°F.</u>	<u>psig</u>	
8	625	550	1.15
9	525	550	11.32
10	475	550	0.87
11	425	550	35.07

12 The above data show that nickel-molybdenum and iron-molybdenum are also effective catalyst in the carbon monoxide reaction.

15 EXAMPLE 5

16 The experiment of Example 1 was again repeated to show the effect of different non-noble metal catalyst constituents. The data are reported in Table V.

19 TABLE V

20	Run No.	12	13	14
21	Metals	CoV	CoCr	CoW
22	Alkali	Cs Acetate	Cs Acetate	Cs Acetate
<u>% CO in Product</u>				
24	Temp.	Pressure		
25	<u>°F.</u>	<u>psig</u>		
26	625	550	7.18	17.24
27	525	550	46.08	22.93
				42.41

28 The above data show the effectiveness of vanadium, chromium, and tungsten as catalysts when used with cobalt.

30 EXAMPLE 6

31 The experiment of Example 1 was repeated to show the effects of using the cobalt-molybdenum in the absence of the alkali metal.

34 TABLE VI

35	Run No.	15
36	Metals	CoMo
37	Alkali	None

<u>% CO in Product</u>		
<u>2 Temp.</u>	<u>3 °F.</u>	<u>Pressure</u> <u>psig</u>
4 625		550 1.08
5 525		550
6 475		550
7 425	550	38.71
8 425	200	47.19

9 The above table shows that the cobalt molybdenum
 10 component alone is only one hundredth as effective (based on
 11 first order reaction rates) as when it is used with cesium
 12 acetate or carbonate. (See Run 1, Example 1 and Run 7, Example
 13 3).

14 EXAMPLE 7

15 Run 1 of Example 1 was repeated to determine the
 16 effect of sulfiding on the effectiveness of the catalyst on
 17 feeds containing sulfur as well as on sulfur-free feeds. The
 18 following results were obtained at 625°F.

19 TABLE VII

20 Run No.	16	17	18
21 Catalyst	Unsulfided	Sulfided in situ	Presulfided
23 Feed			
24 H ₂	45.9	46.44	45.9
25 CO	54.1	52.51	54.1
26 H ₂ S	0	1.4	0
27 Product			
28 CO	17.32	1.19	1.18
29 CO Conversion %	57.9	96.5	96.7

30 The above data show that the sulfided catalyst whe-
 31 ther sulfided in situ (Run No. 17) or presulfided with no sul-
 32 fur in the feed (Run No. 18) gives equilibrium conversions of
 33 carbon monoxide while the unsulfided catalyst with no sulfur
 34 in the feed (Run No. 16) gives much poorer conversion.

35 EXAMPLE 8

36 The conditions of Example 1 were repeated with var-
 37 ious catalysts to show the effect of varying the type of
 38 support, using a low surface area alpha Al₂O₃, faujasite, and
 39 carbon as compared to the high surface area gamma alumina of
 40 Run 2 (Example 1).

TABLE VIII

1	2	19	20	21
2 Run No.	3 Support	4 γ -Al ₂ O ₃	5 Faujasite	6 γ -Al ₂ O ₃
7 Metals	8	9 CoMo (3.5% CoO 13% MoO ₃)	10 CoMo (3.7% CoO 13.8% MoO ₃)	11 CoMo (1.6% CoO 6.0% MoO ₃)
12 Alkali	13	14 Cs Acetate	15 Cs Acetate	16 Cs Acetate
17	18	19	20	21
9 Temp.	10	11 Pressure °F.	12 psig	13 % CO in Product
14	15	16	17	18
19 625	20 550	21 1.17	22 1.15	23 1.18
24 525	25 550	26 0.54	27 0.62	28 0.51
29 475	30 550	31 0.40	32	33 (<1.03)
34 425	35 200	36 0.23	37 32.3	38
39 350	40 200	41	42	43
44 350	45 0	46 41.35	47	48

18 EXAMPLE 9

19 When a catalyst containing sodium carbonate and a
 20 cobalt-molybdenum on alumina hydrogenation-dehydrogenation
 21 catalyst is used according to Example 1 at 600°F. the CO is
 22 substantially completely converted to the thermodynamic equili-
 23 brium concentration of CO₂.

24 EXAMPLE 10

25 A gas mixture consisting of approximately 46% hydro-
 26 gen, 53% carbon monoxide and about 1% H₂S was used as a feed
 27 gas. This gas feed was passed through a catalyst containing
 28 reactor at 550 psig at such a rate as to maintain an exit dry
 29 gas product rate of 2700 V/V/Hr. under conditions of room
 30 temperature and 1 atmosphere of pressure, and together with the
 31 feed gas was fed steam in the mole ratio of 1 mole per mole of
 32 dry product gas. The cobalt-molybdenum used in this experiment
 33 was prepared in the same manner and had the same percentage
 34 composition as that used in Example 1. This cobalt-molybdenum
 35 component was impregnated with an aqueous solution of potassium
 36 carbonate (K₂CO₃) in an amount equivalent to 8.7 x 10⁻⁴ moles
 37 per cc catalyst volume, and was dried at about 150°C. Based on
 38 total catalyst composition there was 13.6 weight percent

1 potassium carbonate. The catalyst was then sulfided by means
 2 of a standard method. The following results were obtained.

3 TABLE IX

4	5	6	Reaction	% CO in Product	
			Pressure	Found	Thermodynamic
			(psig)	Equilibrium	
7	550		550	0.64	0.63
8	425		200	0.20	0.22

9 The above data show the clear advantage of employing
 10 the potassium carbonate on the hydrogenation-dehydrogenation
 11 component.

12 EXAMPLE 11

13 A series of tests were conducted to demonstrate the
 14 criticality of employing an alkali metal material as a shift
 15 catalyst constituent as opposed to utilizing related alkaline
 16 earth metal materials. In each of the tests the alkali or
 17 alkaline earth metal composition was impregnated upon a base
 18 catalyst composed of 3.5 wt. % cobaltous oxide and 13.0 wt. %
 19 molybdenum oxide on gamma-alumina. The base catalyst was from
 20 20-40 U.S. standard screen mesh size. Thirty cubic centimeters
 21 of each of the catalyst materials were charged into a small
 22 cylindrical reactor having a 10:1 length to diameter ratio. The
 23 reactor was positioned within a sand bath.

24 In each of the tests a carbon dioxide-free gas mix-
 25 ture composed of approximately 52 volume % carbon monoxide, 47
 26 volume % hydrogen, and about 1 volume % hydrogen sulfide was
 27 employed as the process reagent. All the tests were conducted
 28 at a temperature of about 425°F. at a reaction zone pressure
 29 of about 200 psig. The gas reagent was passed through the re-
 30 actor at a rate such as to maintain an exit dry gas product
 31 rate of 2700 volumes of gas/volume of catalyst/hour measured
 32 at room temperature and atmospheric pressure. Steam was intro-
 33 duced into the shift reactor in a mole ratio of 1 mole of steam

1 per mole of dry product gas.

2 After charging the catalyst to the reactor, the cata-
 3 lyst was sulfided by passing the feed gas mixture over the
 4 catalyst for about 110 minutes at 250°F. and atmospheric pres-
 5 sure. Thereafter the catalyst bed was gradually heated from
 6 250°F. to 625°F. over a period of 135 minutes while continuously
 7 being contacted with feed gas mixture at atmospheric pressure.
 8 The 625° temperature level was then maintained for an additional
 9 130 minutes while continuing to contact the catalyst with the
 10 gas mixture at atmospheric pressure. All of these operations
 11 were conducted at a gas rate of about 1.33 liters per minute.
 12 Thereafter, the reaction zone pressure was raised to 75 psig
 13 and feed gas introduced into the system at 625°F. for 30 minutes
 14 at a gas rate of about 2.66 liters per minute. The reactor was
 15 then pressurized to 550 psig and the feed gas introduced at a
 16 rate of 2.66 liters per minute for an additional 60 minutes
 17 while the reaction zone was maintained at 625°F. Finally,
 18 steam with feed gas was passed through the system at 625°F. and
 19 then at 525°F.

20 Following this sulfiding procedure, the reactor was
 21 brought to the process conditions enumerated above. The effec-
 22 tiveness of each catalyst was ascertained by analyzing the pro-
 23 cess effluent for CO conversion. Two tests were conducted for
 24 each catalyst over duplicate time periods of about 20 to 45
 25 minutes each. The results of the tests are set forth in Table
 26 X below.

27 TABLE X

28 <u>Alkali or Alkaline</u>	29 <u>Earth Component</u>	30 <u>Amount Component Used</u>	31 <u>% CO</u>
		32 <u>Conversion(d)</u>	33 <u>(b)</u>
30 <u>K₂CO₃</u>	31	4.79 grams/40 cc of base catalyst volume (a)	32 99.4
32 <u>None</u>			33 47.1
33 <u>Mg(OOCH)₂</u>	34	5.26 grams/40 grams of base catalyst(c)	34 48.7

1	Sr(OH) ₂	4.20 grams/40 cc base catalyst volume	16.6
3	Ba(OH) ₂ · 8H ₂ O	16.4 grams/40 cc base catalyst volume	26.9

5 (a) Corresponds to about 15-16 wt. % K₂CO₃. Forty cubic
 6 centimeters of absolutely dry base catalyst weighs
 7 about 26.95 grams.

8 (b) Thermodynamic equilibrium.

9 (c) Corresponds to about 52.5 cc of base catalyst.

10 (d) Approximate average values.

11 The data presented in Table X clearly demonstrates
 12 that alkaline earth metal compositions are substantially less
 13 effective catalyst components as compared with potassium car-
 14 bonate. In fact, the strontium and barium catalyst materials
 15 were substantially ineffective as they served to diminish the
 16 catalyst activity associated with the supported cobalt and
 17 molybdenum materials when used without an alkali metal co-
 18 catalyst.

19 EXAMPLE 12

20 Tests were conducted to ascertain the effect of add-
 21 ing an alkali metal compound, specifically potassium carbonate,
 22 to commercially employed Girdler G-3B iron-chromia shift
 23 catalysts. The iron-chromia catalyst was not analyzed but was
 24 believed to be made up of about 15 wt. % chromia and the bal-
 25 ance iron oxide. One portion of the catalyst was impregnated
 26 with potassium carbonate in the amount of 4.79 grams of potas-
 27 sium carbonate per 40 cc's of iron-chromia base catalyst. The
 28 catalyst materials were then tested for their ability to con-
 29 vert carbon monoxide. The apparatus described in Example 11
 30 was used in the tests.

31 In the tests, which were conducted at 625°F. and 550
 32 psig pressure, the catalysts were presulfided using the pro-
 33 cedure of Example 11 and were contacted thereafter with a feed
 34 gas mixture comprising 1.09 volume % hydrogen sulfide, 45.12

1 volume % hydrogen, and 52.3 volume % carbon monoxide. The gas
2 was introduced into the reaction zone at a rate sufficient to
3 maintain an exit dry gas product rate of 1.33 liters per min-
4 ute at room temperature. This corresponds to about 1.21 liters
5 per minute at standard conditions. About 1.00 cubic centi-
6 meter of water was introduced into the reaction zone as high
7 temperature steam per minute.

8 The conventional iron-chromia catalyst and the potas-
9 sium carbonate promoted iron-chromia catalyst were each sub-
10 jected to three separate test runs totaling two hours duration.
11 The conventional iron-chromia catalyst, that was not promoted
12 with any carbonate material, served to convert, based on an
13 average of the three runs, about 67.3 mole % of the carbon
14 monoxide fed to the reactor. In contrast, the iron-chromia
15 catalyst containing the potassium carbonate promoter served to
16 convert only 42.2 mole % of the carbon monoxide fed to the
17 reactor based upon an average of the three runs conducted with
18 the catalyst. This result was most surprising since, as
19 demonstrated in previous examples, closely related metal com-
20 positions such as cobalt-molybdenum, cobalt-vanadium, cobalt-
21 chromium, iron-molybdenum, nickel-molybdenum are effective
22 shift conversion catalysts at the temperatures and pressures
23 employed in this example when used in conjunction with an
24 alkali metal composition.

25 EXAMPLE 13

26 A series of tests were conducted to demonstrate the
27 criticality of the ratio of hydrogenation-dehydrogenation com-
28 ponent to alkali metal compound present in the catalyst system
29 of the present invention. In the tests, the cobalt oxide-
30 molybdenum oxide gamma-alumina base catalyst described in
31 Example 11 was impregnated with varying amounts of potassium
32 carbonate or cesium carbonate and the activity of the catalyst

1 tested under various conditions of temperature and pressure
2 with feed streams containing carbon monoxide, hydrogen and
3 hydrogen sulfide. Additionally, the activity of commercial
4 iron-chromia catalysts was determined under similar conditions.
5 Finally, comparisons were made with respect to catalysts that
6 were presulfided prior to use using the procedure described in
7 Example 11 and with catalysts that were not contacted with a
8 sulfur composition prior to the commencement of the shift re-
9 action. In the case of the catalyst materials that were not
10 presulfided prior to use, all of the catalysts were contacted
11 with some 5 - 10 cc's of water as high temperature steam prior
12 to contacting a catalyst with the process reagents under shift
13 reaction conditions.

14 The results of the tests are set forth in the attached
15 Figure. The relative catalyst activity values depicted in the
16 Figure were assigned by comparing the reaction rates encountered
17 with the use of the various catalysts at partial conversion con-
18 ditions and assuming a first order reaction with respect to car-
19 bon monoxide conversion.

20 As can be seen in the Figure, a dramatic increase in
21 the relative activity of the various catalysts was encountered
22 when the weight ratio of the hydrogenation-dehydrogenation com-
23 ponent, calculated as a metal oxide, with respect to the alkali
24 metal component, calculated as oxide, was decreased from a
25 value of about 10:1, or conversely, when the weight amount of
26 alkali metal compound on the catalyst was increased relative
27 to the weight of the base material plus the hydrogenation-de-
28 hydrogenation component. The Figure also illustrates that the
29 presence of small amounts of alkali compound (0.6 wt. % K₂O)
30 on the catalyst has a negligible effect on catalyst activity.
31 The data presented clearly demonstrates the critical nature of
32 the weight ratios of the hydrogenation-dehydrogenation component

1 relative to the alkali metal oxide component of the catalyst.
2 The Figure also illustrates that presulfiding the non-noble
3 metal containing shift catalyst prior to use has a substantial
4 beneficial effect on catalyst performance.

5 EXAMPLE 14

6 A final series of tests were conducted to demonstrate
7 the suitability of catalysts made up of noble metals in com-
8 bination with an alkali metal compound for promoting the shift
9 reaction. In each test a 30 cc catalyst charge was contacted
10 in the apparatus described in Example 11 with a gas mixture com-
11 posed of approximately 51 volume % carbon monoxide and 49 volume
12 % of hydrogen. The gas mixture was introduced into the reactor
13 at a rate sufficient to maintain an exit dry gas rate at room
14 temperature of 1.33 liters per minute. This rate corresponds
15 to 1.21 liters per minute at standard conditions. One cubic
16 centimeter of water was introduced into the system per minute
17 as high temperature steam. Both the feed gas and steam were
18 passed over a zinc oxide bed prior to entry into the reaction
19 zone to remove any hydrogen sulfide contained in the feed gas.

20 With the exception of the 5 wt. % palladium on alumina
21 catalyst (a commercially available composition), the noble metal
22 catalysts were prepared by impregnating the support material
23 with a sufficient amount of a noble metal salt contained in
24 water solution to secure the desired amount of noble metal on
25 the support. Thereafter, the metal containing support material
26 was calcined in order to convert the water soluble noble metal
27 salt to the corresponding oxide. Finally, the noble metal-
28 containing catalyst was impregnated with an aqueous solution
29 of potassium carbonate and the total system dried at a tempera-
30 ture varying from 100°- 150°C. Except as indicated, all cata-
31 lysts contained potassium carbonate in amounts corresponding
32 to 0.00174 gram atoms of potassium per cubic centimeter of

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- 1 base, in the case of non-metal containing catalysts, or base
- 2 plus metal, in the case of noble metal-containing catalysts.
- 3 The results of the tests are set forth in Table XI below.

TABLE XI

TABLE XI - (Continued)

22 (a) No calcination after platinum impregnation.

1 As can be seen by referring to Table XI, the noble
 2 metal based compositions possess significant catalytic activity
 3 for promoting the shift reaction. High activity is shown when
 4 a given catalyst serves to convert significant amounts of the
 5 CO in the gas stream at relatively mild temperature and pres-
 6 sure conditions.

7 EXAMPLE 15

8 A catalyst was prepared similar to that of Example
 9 10 except that 8.7×10^{-4} moles of sodium carbonate per cubic
 10 centimeter of base plus cobalt oxide and molybdenum oxide was
 11 used instead of potassium carbonate. The catalyst was presul-
 12 fided prior to use following the procedure of Example 11 and
 13 was subsequently used, following the procedure of Example 10,
 14 to treat, under shift conditions, a reagent stream containing
 15 50.68 volume % hydrogen, 48.97 volume % carbon monoxide, 0.02
 16 volume % carbon dioxide and 1.04 volume % hydrogen sulfide.
 17 The effluent from the shift reactor was analyzed for carbon
 18 monoxide content to determine the activity of the catalyst.
 19 The results of the tests are set forth in Table XII.

20 TABLE XII

21 Temperature 22 (°F.)	23 Pressure (psig)	Volume % CO contained in dry product gas	% CO Conversion
24 625	25 550	1.23	96.4
25 525	26 550	0.50	98.5
26 425	27 200	0.20	99.4
27 350	100	14.12	62.2

28 The above data clearly demonstrate that sodium com-
 29 pounds, in particular, sodium carbonate, is a highly effective
 30 shift catalyst component.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A process for the conversion of carbon monoxide and steam to hydrogen and carbon dioxide which comprises contacting said carbon monoxide and steam under shift reaction conditions with a catalyst comprising: (i) an alkali metal compound derived from an acid having an ionization constant less than 1×10^{-3} and (ii) a hydrogenation-dehydrogenation component selected from the group consisting of ruthenium, palladium, osmium, iridium, platinum, and mixtures thereof, the weight ratio of said hydrogenation-dehydrogenation component, calculated on the basis of the oxide thereof, to said alkali metal compound, calculated on the basis of the oxide thereof, being in the range of from about 0.001:1 to about 10:1.
2. The process of claim 1 wherein said alkali metal compound is an alkali metal carbonate.
3. The process for the conversion of gas mixtures containing carbon monoxide and steam and being substantially free of a sulfur material to hydrogen and carbon dioxide which comprises contacting said gas mixture substantially in the vapor phase and under shift reaction conditions with a catalyst comprising: (i) an alkali metal compound derived from an acid having an ionization constant less than 1×10^{-3} , and (ii) a hydrogenation-dehydrogenation component comprising a noble metal of Group VIII of the Periodic Table and mixtures thereof, the weight ratio of said noble metal hydrogenation-dehydrogenation component, calculated on the basis of the oxide thereof, to said alkali metal compound, calculated on the basis of the oxide thereof, being in the range of about 0.0001:1 to about 10:1.
4. The process of claim 3 wherein said catalyst is contained on a support material.

5. The process of claim 3 wherein said alkali metal compound is an alkali metal carbonate.
6. The process of claim 4 wherein said alkali metal compound is potassium carbonate.
7. The process of claim 6 wherein said support is alumina.
8. An improved catalyst composition comprising, in combination, (i) an alkali metal compound derived from an acid having an ionization constant less than 1×10^{-3} and (ii) a hydrogenation-dehydrogenation component comprising a noble metal constituent selected from the group consisting of ruthenium, palladium, osmium, iridium, platinum, and mixtures thereof, the weight ratio of said hydrogenation-dehydrogenation component, calculated on the basis of the oxide thereof, to said alkali metal compound, calculated on the basis of the oxide thereof, being in the range of from about 0.0001:1 to 10:1.
9. The catalyst compositions of claim 8 contained on a support material.
10. The catalyst composition of claim 9 wherein the support is alumina.
11. The composition of claim 8 wherein said alkali metal compound is an alkali metal carbonate.
12. The composition of claim 9 wherein said alkali metal compound is potassium carbonate.
13. A process for the conversion of carbon monoxide and steam to hydrogen and carbon dioxide which comprises contacting said carbon monoxide and steam under shift reaction conditions with a catalyst comprising: (i) an alkali metal compound derived from an acid having an ionization constant less than

1×10^{-3} and (ii) a hydrogenation-dehydrogenation component comprising a noble metal constituent selected from the group consisting of ruthenium, palladium, osmium, iridium, platinum, and mixtures thereof, the weight ratio of said hydrogenation-dehydrogenation component, calculated on the basis of the oxide thereof, to said alkali metal compound, calculated on the basis of the oxide thereof, being in the range of from about 0.0001:1 to about 10:1.

14. The process of claim 13 wherein said alkali metal compound is an alkali metal carbonate.

15. The process of claim 14 wherein said alkali metal carbonate is potassium carbonate.

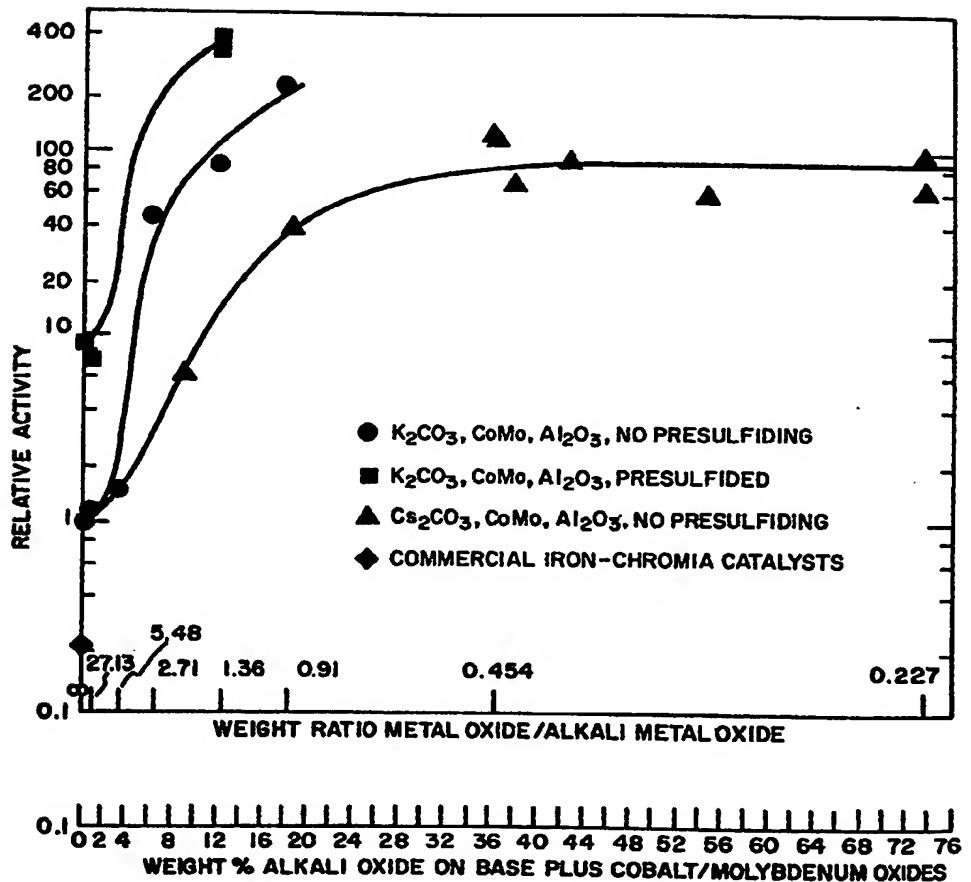
16. The process of claim 13 wherein said catalyst is contained on a support material.

17. The process of claim 16 wherein said support is alumina.

18. The process of claim 13 wherein said process is conducted at a temperature in the range of 300 to 700°F.

19. The process of claim 13 wherein said process is conducted at a pressure varying from about 200 to 3000 psig and at a space velocity of at least 300 volumes of gas mixture per volume of supported catalyst per hour.





PATENT AGENTS